

# Determination of Densities of Amino Compounds for Molar Volumes in Aqueous Solutions with Magnetic Float Densimeter at Various Temperatures

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**Abstract.** Densities ( $\rho$ ) of urea ( $\text{H}_2\text{NCONH}_2$ ), methylurea ( $\text{H}_3\text{C-HNCONH}_2$ ), melamine ( $\text{C}_3\text{N}_6\text{H}_6$ ) in aqueous, along with methylurea in  $0.05 \text{ mol kg}^{-1}$  aqueous urea solutions have been measured with magnetic float densimeter (MFD) with the accuracy value of  $1 \times 10^{-3} \text{ kg m}^{-3}$ . The data were used to calculate apparent molar volumes ( $V_\phi$ ) that are compared with the values obtained with Anton Paar densimeter DMA 60/601 model. The values of the  $\rho$  and  $V_\phi$  parameters were regressed and extrapolated to zero concentration ( $m = 0$ ), for their limiting densities ( $\rho^\circ$ ) and limiting molar volumes ( $V_\phi^\circ$ ) along with their respective slope values. The values of the  $\rho^\circ$  and  $V_\phi^\circ$  constants elucidated the heteromolecular interactions of  $-\text{NH}_2$  group, and it was noted that  $-\text{NH}_2$  in different chemical compounds influenced interactions with water, especially with electron donating  $-\text{CH}_3$  group of methylurea.

**Keywords:** magnetic float densimeter, Anton Paar, heteromolecular interactions, hydrophilic interactions, hydrophobic interactions, molar volume, densities of urea/methylurea, melamine

## Introduction

The exclamation of 'eureka' by Archimedes in 1778, after experiencing buoyancy in his body weight in water meant the fulfilment of his pursuit of knowing purity of gold as it gave a hope to determine density that fascinated him a lot (Romero and Paez, 2006). His concept, later boosted the industrial processes of metallurgical extraction and separation (Robert, 1952). This led to the development of an instrument based on buoyancy, referred to as magnetic float, which is used for the measurement of density of solutions of organic compounds consisting of amino ( $-\text{NH}_2$ ) functional groups. As the  $-\text{NH}_2$  group introduces several physicochemical properties in compounds, it is used as a probe to derive reliable information on solute-solute and solute-solvent interactions (Apelblat and Manzurola, 1999). The  $-\text{NH}_2$  group is an important component of amino acids, peptides, proteins and several other biochemicals. Activities of the  $-\text{NH}_2$  group depend on its chemical environment. The thermodynamic studies of amino compounds are not sufficiently reported (Cabani *et al.*, 1972). The present studies were thus undertaken on the  $\rho$  and  $V_\phi$  parameters of melamine (an important constituent of amino plastic polymers), urea and methylurea, along with methylurea in  $0.05 \text{ mol kg}^{-1}$  aqueous urea.

The effects of  $-\text{NH}_2$  groups on heteromolecular and pair-wise interactions have been analyzed (Nelson and Cox, 2002). A highly accurate densimeter, with 1 ppm variation in the  $\rho$  for calculation of the  $V_\phi$  values, is required for these studies

(Fernandez *et al.*, 1982; Friedman and Krishnan, 1973). Pycnometer and dilatometer measure the  $\rho$  values with  $1 \times 10^{-4} \text{ g cm}^{-3}$  accuracy, which do not yield sufficiently accurate data for the calculation of  $V_\phi$  values (Lee and Millero, 1995; Hershey *et al.*, 1983). The accuracy, however, depends on the accuracy of the balance, which measures the weights of the solutions. Anton Paar (vibrating digital tube, DMA model 60/601 gives  $1 \times 10^{-6} \text{ g cm}^{-1}$  variation) measures the  $\rho$  values with  $1 \times 10^{-6} \text{ g cm}^{-3}$  (Singh, 2005). This instrument is expensive, and complicated in maintenance and repair. Magnetic flow densimeter (MFD) is, therefore, preferred, which is simple to operate in all respects (Millero, 1967). This instrument is based on the buoyancy principle of Archimedes. It consists of a magnetic float (Millero, 1970; 1968) that hovers in the solutions and an electromagnetic interaction is generated separately (Millero *et al.*, 1972) by solenoids  $S_1$  and  $S_2$  that control the movements of the float inside the solution in the cell (Millero *et al.*, 1978). Recently, the density and viscosity measurements of aqueous solutions of biomolecules have been found to be very useful to illustrate solute-solvent interactions (Singh and Sharma, 2006). Such studies have been noted to authentically illustrate the denaturation and unfolding dynamics of the proteins, as the densities of the solutions also decide the behaviour of partition of certain medically important molecules in different immiscible phases (Singh and Sharma, 2006).

In consideration of these aspects, studies were undertaken to determine densities ( $\rho$ ) of urea, methylurea, melamine in aqueous, along with methylurea in aqueous urea solutions, using

magnetic float densimeter. The data were used to determine their apparent molar volumes.

## Materials and Methods

**Instrumental description.** The magnetic flow densimeter (MFD) is a simple and economical instrument, at par in accuracy with Anton Paar, in which the bar magnet (5 x 35 mm) is fixed in the cylindrical tube of the float, and thus called magnetic float densimeter (MFD). A sketch diagram of MFD has been shown in Fig. 1. The present model of the

float is made of glass material that contains an upper bulb of 30 mm dia with upward protrusion of 15 mm, and below the bulb is a cylindrical tube, 70 mm long, with a tapered lower-end (Fig. 1). In this tube is fitted, a bar magnet (25 mm long x 5 mm dia). The MFD contains a cell C with the standard joint of B55/60 at the top of the bulb C of 50 mm dia. Below the bulb C, there is attached a glass tube  $T_2$ , which is 95 mm in length and 15 mm inner dia. The  $T_2$  fits into the standard joint of the vessel A. The vessel A consists of a glass tube T, 90 mm long and 20 mm dia. The minor ( $S_2$ ) and

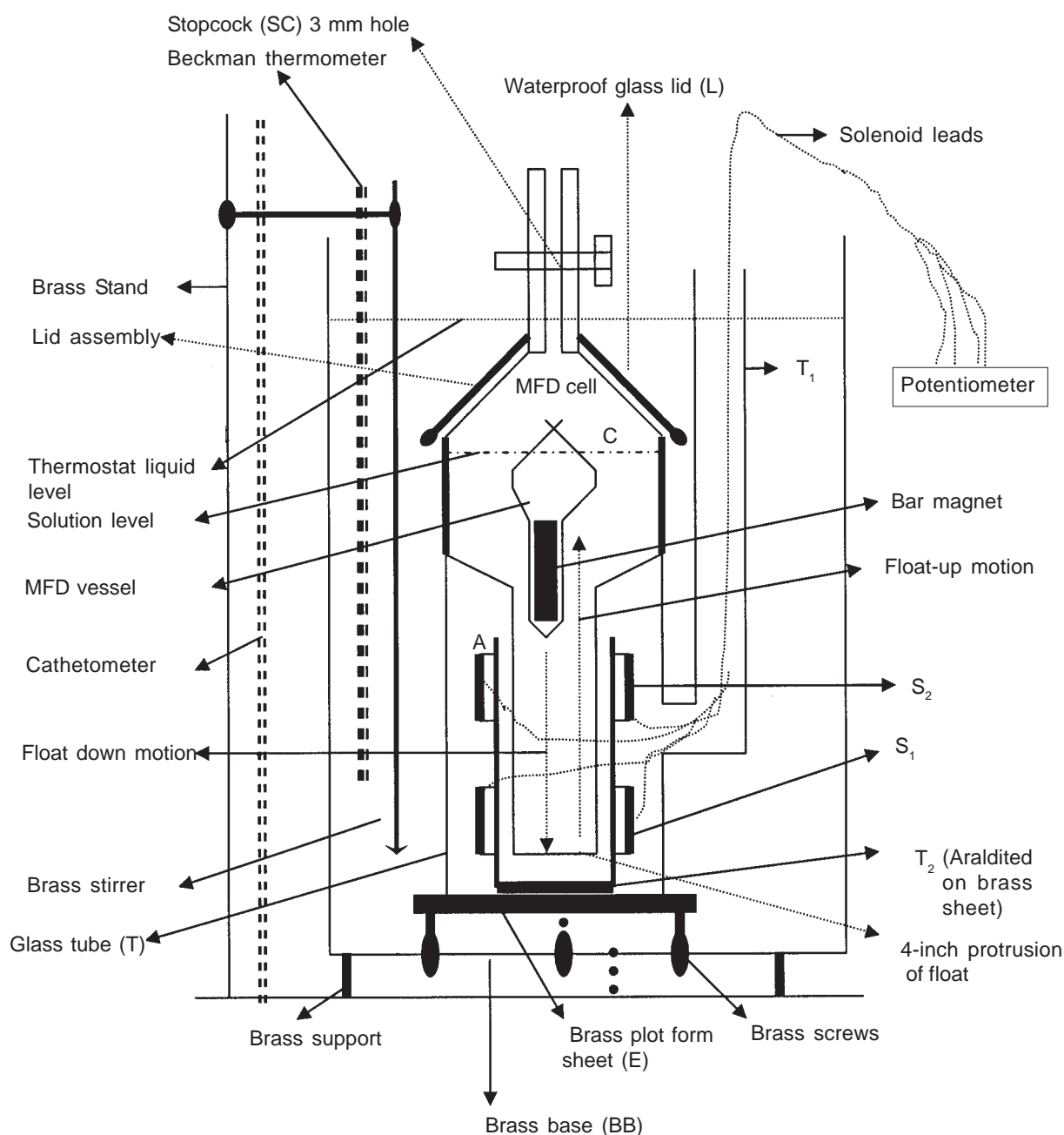


Fig. 1. Sketch diagram of magnetic float densimeter (MFD).

major ( $S_1$ ) solenoids of 15 turns with  $1.5 \Omega$  (ohm), and 730 turns with  $15.4 \Omega$  (ohm), respectively, of enameled insulated copper wire of 29 number are fixed with Araldite on the outer surface of  $T_2$ , at 30 mm distance from each other. Current in  $S_2$  and  $S_1$  induces electromagnetic interactions to generate magnetic force for pulling the float down, touching the bottom of the tube  $T_2$  (Fig. 2a). The MFD cell C is inserted into B55/60 joint at the top of glass vessel A, 105 mm long with 55 mm dia. Silicon grease is applied to avoid leakage. The vessel A is also fixed with Araldite on brass platform E, fixed on brass base (BB) with leveling screws. A glass side tube  $T_1$ , 9 inch long and 10 mm dia is attached on the cylindrical glass vessel A for solenoid leads. Initially,  $\pm 30 \times 10^{-3} \text{dm}^3$  of solvent/solution is taken in bulb C for measurement, and later the float is inserted through the lid, L. The subsequent stock solutions are added through the 3 mm hole of stopcock, SC (Fig. 1) through a 20 cm long, 2 mm internal dia Teflon tube attached to a 10 ml syringe. The float of  $20.66143 \text{ cm}^3$  and  $0.971214 \text{ g cm}^{-3}$  at 298.15 K hovers on solution of  $0.940022$  to  $1.500002 \text{ g cm}^{-3}$  (Fig. 2b). However, rings of 100% platinum, of specified weights, are added on top of the float to vary its density. The float assembly is kept in the thermostated waterbath and levelled with screws. The  $\pm 0.01^\circ \text{C}$  temperature control is maintained, read with Beckman thermometer. The stirring is done with a brass stirrer. Freshly and fully charged, two 12 volt lead batteries are connected in parallel for constant DC current supply to  $S_1$ . A 2 volt battery is connected to  $S_2$  (Fig. 2c). A Leeds and Northrop potentiometer, across a standard resistor of  $1 \Omega$  (Leeds and Northrop) is used to measure the current (Fig. 2c). The current in  $S_2$  brings the float to the field of the  $S_1$  against a buoyant force (BF) of the liquid. The lower coloured tip of the float anchors on the inner base of the cell C. The float weight  $W_f$  and volume  $V_f$  displace  $V$  ml of liquid of density ( $\rho$ ) as  $\text{g cm}^{-3}$ , and BF of the displaced liquid opposes a downward motion of the float as under:

$$\rho_f V_f = -W_f \quad (1)$$

Addition of Pt rings of the weight  $W_{\text{Pt}}$  and volume  $V_{\text{Pt}}$  give the following relation:

$$(\rho_f V_f + \rho_{\text{Pt}} V_{\text{Pt}}) = (W_f + W_{\text{Pt}}) \quad (2)$$

The  $S_1$  current ( $i$ ) generates EMF (electromagnetic force) on  $W_f$  to hold the float down (Fig. 2a) and the current ( $i$ ) decreases (Fig. 2c), till float is released; the relation is expressed as under:

$$(\rho_f V_f + \rho_{\text{Pt}} V_{\text{Pt}}) = (W_f + W_{\text{Pt}}) + F_m i \quad (3)$$

The  $\rho_f$  and  $\rho_{\text{Pt}}$  ( $2.4820 \text{ g cm}^{-3}$  at  $25^\circ \text{C}$ ) are the float and platinum densities, respectively.  $V_f$ , the float volume and  $W_{\text{Pt}}$  are con-

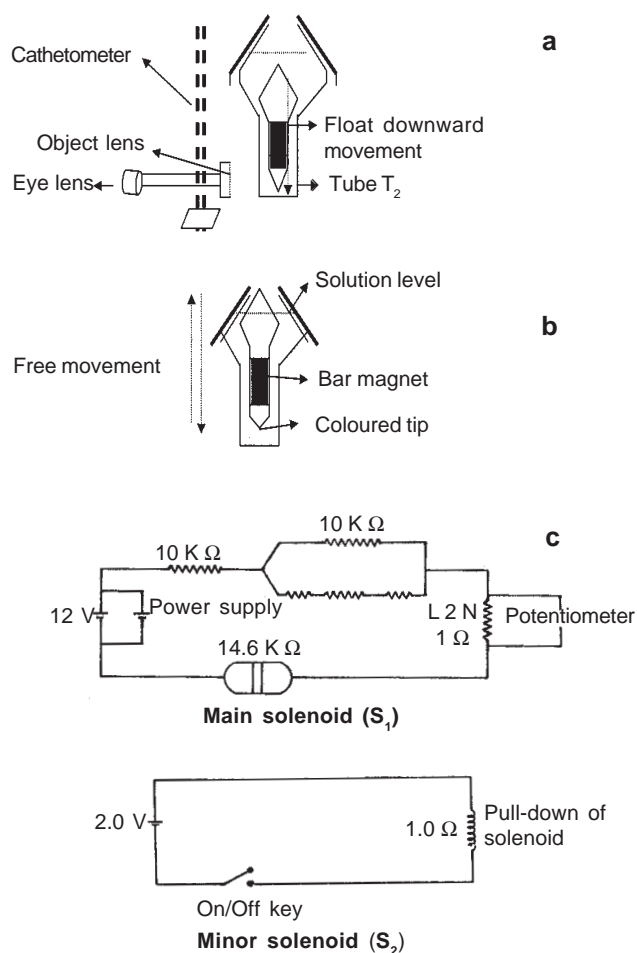
stant factors ( $m$ ). The current ( $i$ ) is the float holding current and  $F_m$  is the force factor of the magnet. The float with platinum rings replaces the solution, which is taken into account as under:

$$\rho_{\text{soln}} (V_f + V_{\text{Pt}}) = -(W_f + W_{\text{Pt}}) + F_m i \quad (4)$$

The relation is simplified as:

$$\rho_{\text{soln}} = \left( \frac{W_f + W_{\text{Pt}}}{V_f + V_{\text{Pt}}} \right) + \left( \frac{F_m}{V_f + V_{\text{Pt}}} \right) \times i \quad (5)$$

The  $\rho_{\text{soln}}$  is the solution density;  $(W_f + W_{\text{Pt}})/(V_f + V_{\text{Pt}})$  is  $\rho_f$ , the float density; and  $F_m/(V_f + V_{\text{Pt}})$  is the solenoid constant  $S$ , and their values are calculated from an intercept and slope of the



**Fig. 2.** Sketch diagram of operational functions of the magnetic float densimeter: (a) pulling and holding down of the magnetic float through the supply of current in  $S_2$  and  $S_1$  which induces magnetic interactions to generate magnetic force for pulling the float down; (b) hovering of magnetic float in the solution; (c) supply of current and the placement of potentiometer across solenoids.

$W_{Pt}$  versus potential drop with the known values of density. From the known values,  $(W_f + W_{Pt})$ , are calculated the  $V_f$  values using the following relation:

$$V_f = (W_f + W_{Pt})/\rho_f \quad (6)$$

After calibration with known density, the density is determined and used to calculate apparent molar volume ( $V_\phi$ ) from the relation.

**Operational conditions of MFD and the materials used.** The float was selected for a certain range of densities of the solutions. For example, the float used in the present study was found to work for the solutions of 0.94002 to 1.50000 g cm<sup>-3</sup>. Since the float must swim on the surface of the solution, its density must be lower than that of the solution selected for density measurements (Millero *et al.*, 1978). The assembly was kept dipped in the waterbath, with the thermostatic temperature control within  $\pm 0.01$  °C. The Beckman thermometer used in the studies was calibrated at the National Physical Laboratory, New Delhi, India. The temperature was maintained by circulating cold water from MK70 cooling machine reservoir through a thick-walled PVC tube fitted to a copper coil immersed in the thermostatic liquid. The immersion rod was encircled to contact thermometer with autotap electric supply relay to balance the decrease in the temperature. The homogeneity in the temperature was maintained by stirring the water of the bath with a brass stirrer and the unit was levelled with screws on BB (Fig. 1).

The  $S_1$  and  $S_2$  were made up of 730 turns of 15.4  $\Omega$  (ohm), and 15 turns of 1.5  $\Omega$  (ohm) of enameled insulated pure copper wire of 29 gauge, respectively. The platinum rings were made of pure platinum (Sigma). NaCl, melamine, urea and methylurea (E. Merck) were used as received. For the making of solutions, w/w, distilled water was used.

**Theory and working.** The float movement was visualized through eye lens of a cathetometer kept at some distance from the unit (Fig. 1; 2a). Thus, the EMF in the circuit (Fig. 2c) increased the gravitational force of the float by  $F_m$  constant times of the current ( $i$ ), in accordance with equation (4):

$$\rho_{soln} (V_f + V_{Pt}) = -(W_f + W_{Pt}) + F_m i \quad (4)$$

The current ( $i$ ) holds down the float, the  $F_m$  is the force factor of the bar magnet, the  $\rho_f$  and  $\rho_{Pt}$  are the float and platinum densities, respectively. The float replaces the  $\rho_f V_f$  mass (the  $\rho_f V_f =$  mass of the replaced liquid) of the solution. Thus, the  $(\rho_f V_f)$ , like  $PV = K$  (Boyle's law), is a constant factor. The loading of the calibrated Pt rings on top of the float facilitates to hold it down in a grip of the magnetic force, which is released on decrease of the current ( $i$ ) of the solenoids. The

2.4820 and 0.99705 g cm<sup>-3</sup> densities of platinum and water at 298.15 K, respectively, were used (Lide, 2003).

**Calibration of the float.** A solution of known density was filled in cell C and the float was inserted smoothly in the solution. The range of the density of the solution, with respect to the density of the float, was chosen in advance. The potential to generate current, current ( $i$ ) was passed in the  $S_2$  to bring the float in the range of the electric field of  $S_1$ . Thus, the float was held at the bottom of tube (T) till the potential was reduced. The potential drop, which just releases the float, was measured with potentiometer (Fig. 2c), and the density of the float was increased by adding the Pt ring of weight,  $W_{Pt}$ . Similar procedure was repeated to measure the potential drop for the addition of each Pt ring of different weights. Separate seven rings were added in an accumulative weight.

**Calculations.** The float + Pt rings replace the solution, thus, the following equation (5) was used as under:

$$\rho_{soln} = \left( \frac{W_f + W_{Pt}}{V_f + V_{Pt}} \right) + \left( \frac{F_m}{V_f + V_{Pt}} \right) \times i \quad (5)$$

Here, the minus sign was neglected as the magnitude of the density was considered. The  $(W_f + W_{Pt})/(V_f + V_{Pt})$  is depicted as  $\rho_f$ , which is the density of the float, and the  $F_m/(V_f + V_{Pt})$  is the solenoid constant depicted as  $S$ , which are calculated from the intercept and slope values of equation (5) with the known density of the liquid. Thus, the the following equation (6) was obtained by calibrating the float with solution of the known density.

$$V_f = (W_f + W_{Pt})/\rho_f \quad (6)$$

## Results and Discussion

The values of the  $W_{Pt}$ , with the corresponding potential drop, are given in Table 1, and their plot is given in Fig. 3. The assembly and the circuit sketches are drawn in Fig. 1, 2a, 2b, and 2c. For comparison, the densities of the solutions were measured with Anton Paar (AP) by noting the vibrating periods ( $\tau$ ) of the oscillating tube filled with solution (Singh, 2005). The values were calculated from the following equation:

$$\rho_{soln} - \rho_{water} = K (\tau_{soln}^2 - \tau_{water}^2) \quad (7)$$

The densities,  $\rho_{soln}$ ,  $\rho_{water}$ , and the  $\tau_{soln}^2$  and  $\tau_{water}^2$  are the oscillating frequencies ( $\tau$ ) of the borosilicate vibrating tube for solution and water, respectively. The  $K$  is a constant determined with the solution of the known  $\rho$  values. The values of the  $\rho$  of NaCl aqueous solutions were calculated with the MFD and AP from equations (5) and (7), respectively, and of urea, methylurea and melamine with the MFD from equation (5).

These densities were used to calculate the  $V_\phi$  values with equation (8):

$$V_\phi = \frac{1000(\rho_0 - \rho)}{m\rho_0\rho} + \frac{M}{\rho} \quad (8)$$

The molar mass ( $M$ ), molality ( $m$ ), and the  $\rho_0$  and  $\rho$  are the solvent and solution densities, respectively. The experimental data of densities and volumes of aqueous NaCl are given in Table 2, and of urea, methylurea and melamine systems in Table 3. Their regression constants are given Table 4. The  $V_\phi$  values of the systems were fit to equation (9):

$$V_\phi = V_\phi^0 + S_v m \quad (9)$$

**Table 1.** Float weight with platinum rings and the corresponding potential drop measured with potentiometer (Leeds and Northrop)

Potential (mV)	Pt weight (g)
0.0900	0.1675
0.1400	0.1500
0.1825	0.1325
0.2275	0.1200
0.2850	0.1025
0.3250	0.0825
0.3775	0.0650

**Table 2.** Density ( $\rho$ ), g cm<sup>-3</sup> and apparent molal volumes ( $V_\phi$ ), cm<sup>3</sup> mol<sup>-1</sup> of aqueous solution systems at the temperatures of 298.15 K

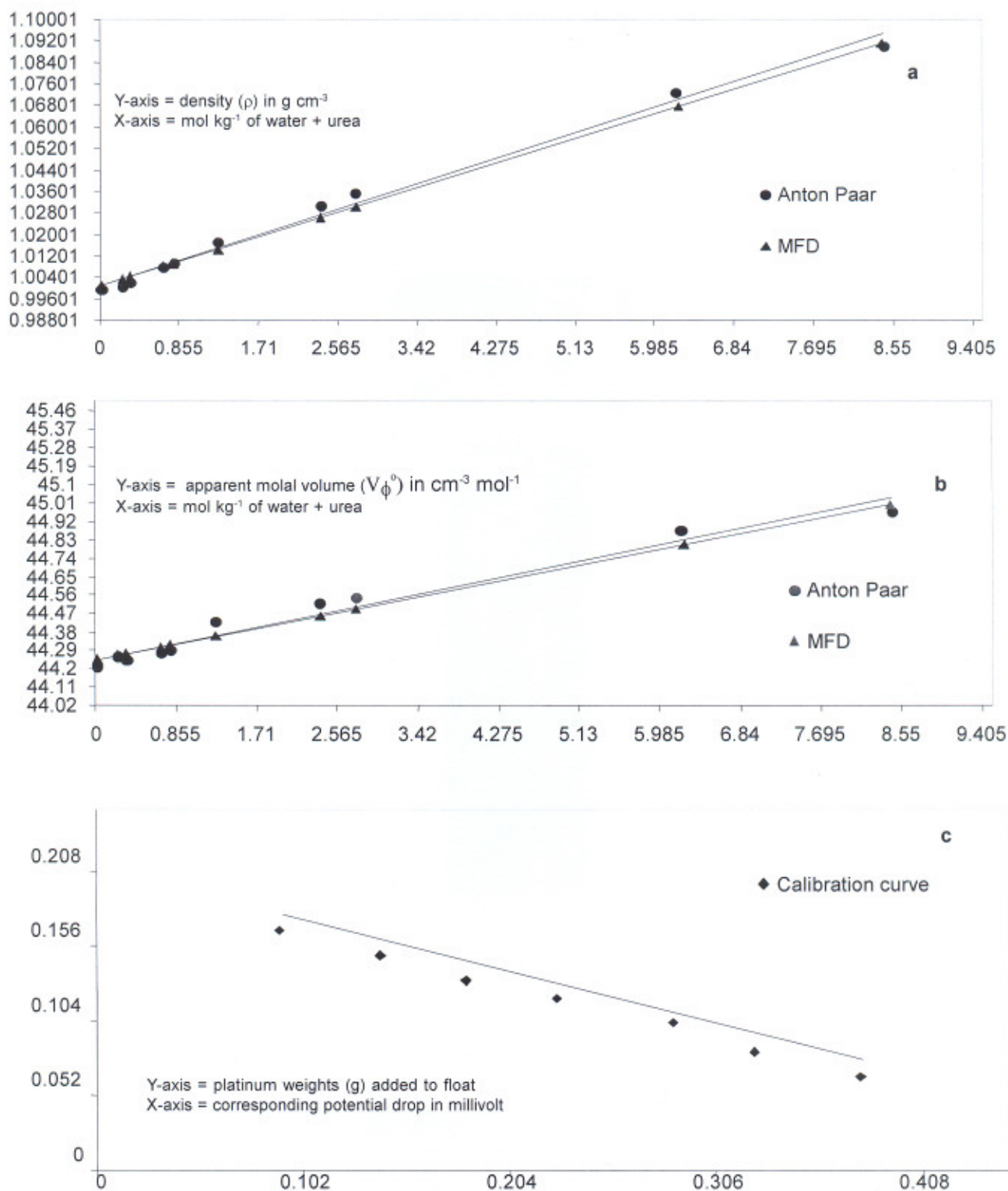
Aqueous NaCl systems at 298.15 K						
m (mol kg <sup>-1</sup> )	$\rho$ with AP	$\rho$ with MFD	$\Delta\rho$	$V_\phi$ with AP	$V_\phi$ with MFD	$\Delta_\phi$
0.0606	0.99815	0.99815	2.00-06	17.03	17.06	-0.03
0.1377	1.00129	1.00129	1.60-06	17.31	17.32	-0.01
0.1715	1.00263	1.00265	-1.80-05	17.55	17.45	0.10
0.1720	1.00259	1.00259	5.70-08	17.90	17.91	0.00
0.1769	1.00278	1.00274	3.70-05	17.95	18.16	-0.21
0.3343	1.00909	1.00908	9.90-06	17.95	17.98	-0.03
0.7816	1.02627	1.02606	2.10-04	18.66	18.92	-0.27
1.0359	1.03581	1.03592	-1.10-04	18.88	18.78	0.10
1.0367	1.03595	1.03599	-4.30-05	18.78	18.74	0.04
1.5246	1.05348	1.05413	-6.50-04	19.36	18.95	0.42
1.9466	1.06830	1.06760	7.00-04	19.67	20.02	-0.35
2.0870	1.07295	1.07346	-5.10-04	19.85	19.61	0.24
3.0795	1.10555	1.10550	5.10-05	20.49	20.51	-0.02
4.9603	1.16835	1.16789	4.60-04	20.14	20.23	-0.09

$\Delta\rho = \text{AP-MFD}$ , g cm<sup>-3</sup>;  $\Delta_\phi = \text{AP-MFD}$ , cm<sup>3</sup> mol<sup>-1</sup>; AP = Anton Paar; MFD = magnetic float densimeter; m = molality

**Table 3.** Density ( $\rho$ ), g cm<sup>-3</sup>, and apparent molal volumes ( $V_\phi$ ), cm<sup>3</sup> mol<sup>-1</sup>, of solutions of different molalities ( $m$ ) of binary and ternary systems\* at three temperatures

m (mol kg <sup>-1</sup> )	293.15 K		298.15 K		303.15 K	
	$\rho$	$V_\phi$	$\rho$	$V_\phi$	$\rho$	$V_\phi$
<b>Aqueous urea systems</b>						
0.0050	1.00267	44.21	1.00196	44.21	1.00136	44.72
0.0106	1.00273	44.21	1.00202	44.21	1.00142	44.72
0.0150	1.00279	44.21	1.00207	44.21	1.00147	44.72
0.0180	1.00282	44.21	1.00211	44.21	1.00150	44.72
0.0205	1.00285	44.21	1.00214	44.21	1.00153	44.72
0.0255	1.00291	44.21	1.00219	44.21	1.00159	44.72
0.0302	1.00297	44.21	1.00225	44.21	1.00164	44.72
0.0322	1.00299	44.21	1.00227	44.21	1.00166	44.72
0.0355	1.00303	44.21	1.00231	44.21	1.00170	44.72
<b>Aqueous methylurea</b>						
0.0050	0.99834	54.07	0.99714	49.97	0.99544	152.54
0.0106	0.99838	48.44	0.99718	59.33	0.99548	109.47
0.0150	0.99842	56.23	0.99722	62.35	0.99552	90.39
0.0180	0.99844	59.44	0.99724	53.14	0.99554	81.55
0.0205	0.99846	55.36	0.99726	57.23	0.99556	74.77
0.0255	0.99850	60.45	0.99730	60.23	0.99560	70.49
0.0302	0.99854	61.49	0.99733	60.90	0.99564	66.57
0.0322	0.99855	61.60	0.99735	62.14	0.99565	63.83
0.0355	0.99858	61.72	0.99737	62.18	0.99568	63.93
<b>Methylurea in 0.05 mol kg<sup>-1</sup> aqueous urea</b>						
0, solvent	1.00698	44.21	1.00648	44.21	1.00598	44.23
<b>Ternary systems</b>						
0.0050	0.99843	64.26	0.99802	62.13	0.99603	64.32
0.0106	0.99846	64.12	0.99805	62.17	0.99606	64.11
0.0150	0.99848	64.02	0.99807	62.20	0.99609	63.95
0.0180	0.99850	63.95	0.99809	62.22	0.99610	63.84
0.0205	0.99851	63.89	0.99810	62.24	0.99612	63.76
0.0255	0.99854	63.79	0.99812	62.28	0.99615	63.59
0.0302	0.99857	63.69	0.99814	62.32	0.99618	63.45
0.0322	0.99858	63.65	0.99815	62.34	0.99619	63.39
0.0355	0.99860	63.59	0.99817	62.37	0.99621	63.29
0.0500	0.99864	63.34	0.99824	62.50	0.99629	62.91
0.1000	0.99899	62.88	0.99848	63.08	0.99658	62.13
0.1500	0.99940	63.01	0.99872	63.83	0.99687	62.17
0.2500	0.99975	65.04	0.99920	65.84	0.99745	64.75
<b>Aqueous melamine</b>						
0.0050	0.99811	130.98	0.99693	128.37	0.99565	111.45
0.0106	0.99868	105.51	0.99741	88.06	0.99581	105.25
0.0150	0.99913	97.09	0.99780	71.57	0.99593	103.38
0.0180	0.99943	95.20	0.99806	64.47	0.99602	100.96
0.0205	0.99969	90.00	0.99828	60.18	0.99609	89.69
0.0255	1.00020	85.41	0.99871	57.62	0.99624	81.09
0.0302	1.00067	89.60	0.99911	68.95	0.99637	70.96
0.0322	1.00088	85.71	0.99929	71.03	0.99643	66.79
0.0355	1.00122	83.27	0.99957	73.61	0.99653	64.13

\*binary systems = aqueous urea, aqueous methyl urea systems; ternary systems = urea and methyl urea in 0.05 mol kg<sup>-1</sup> solutions



**Fig. 3.** Densities ( $\rho$ ) and apparent molal volumes ( $V_{\phi}^0$ ) measured with Anton Paar and magnetic float densimeter (MFD), and the potential drop with added weight of platinum rings to the float showing an inverse relationship: for (a) and (b), the Y-axis denotes the the densities ( $\rho$ ) and apparent molal volumes ( $V_{\phi}^0$ ), respectively; for (c), the Y-axis represents the values of the platinum weights (g) added to the float and the X-axis represents the corresponding potential drop in millivolt.

The values of the  $V_{\phi}^0$  constant are known as the limiting molar volumes, and the  $S_v$  is the slope value of to elucidate the solute-solvent and solute-solute interactions, respectively. The  $\rho$  data of aqueous NaCl were found to be in close agreement with those reported in literature (Singh and Kumar, 2006). The densities and the volumes of urea obtained with MFD and Anton Paar have been plotted in Fig. 3a and 3b; the latter showing a close agreement between the values measured with the two instruments. The potential drop with added Pt rings to the float showed an inverse relationship, as may be noted from Fig. 3c. This enabled the calibration of the float, i.e., the solenoid constant,  $S$ .

For similar compositions of urea and methylurea systems, the  $\rho$  and  $V_{\phi}^0$  data were higher for the former by  $0.00433 \text{ g cm}^{-3}$ , than those of methylurea at each temperature. The  $\rho$  values of the urea systems decreased by  $7.1 \times 10^{-4}$  and  $6.0 \times 10^{-4} \text{ g cm}^{-3}$  from 293.15 to 298.15 K and 298.15 to 303.15 K, respectively, and of methylurea by  $1.2 \times 10^{-3}$  and  $1.7 \times 10^{-7} \text{ g cm}^{-3}$  at the respective temperatures. The values of the  $\rho$  indicate larger structure-breaking action of urea on bulk water, than that of methylurea, with temperature, which show an influence of the  $-\text{CH}_3$  group, on heteromolecular interactions with water. Thus, the  $-\text{CH}_3$  group affects the activity of  $-\text{NH}_2$  group of methylurea, as the chemical environment of  $-\text{NH}_2$  group was changed in methylurea. For higher temperature, however, both showed larger decrease in the  $\rho$  values (Table 3). The higher  $\rho$  values of urea, than those of the methylurea, confirm stronger heteromolecular forces of urea than of the methylurea. These observation show that the  $-\text{CH}_3$  group weakens molecular forces of methylurea. Hence, urea destabilizes the water structure more strongly, than is done by methylurea, which facilitates the development of a stronger hydrosphere around the  $-\text{NH}_2$  and  $>\text{C}=\text{O}$  groups of urea. Obviously, the methylurea had weaker forces with loosened hydrosphere formation due to hydrophilic interactions caused by  $-\text{CH}_3$ . It thus elaborates that the  $-\text{NH}_2$  of N-ureas with  $-\text{CH}_3$  weakens the structure-breaking action of methylurea.

On the other hand, an activity of the  $-\text{NH}_2$  group of melamine, where it is attached with a conjugated heteroatomic benzene ring system, is observed to be peculiar, as the  $\rho$  values of the melamine were noted to be lower in order of urea > methylurea > melamine. This predicts that the  $-\text{NH}_2$  groups of melamine were not able to establish stronger heteromolecular forces as compared to urea and methylurea. Melamine virtually behaved as a mild structure-breaker with lower internal pressure on the heteromolecular complex. The decrease in  $\rho$  values of urea from 293.15 to 298.15 K was  $4.56 \times 10^{-3}$ , which for methylurea was  $2.3 \times 10^{-4} \text{ g cm}^{-3}$ . It may be concluded that the  $-\text{NH}_2$  group in the conjugated systems develops weaker intermolecular forces with weaker interactions with water, which break the water

structure mildly in the order of urea > methylurea > melamine. It seems that conjugation of melamine ring was weakened by the presence of 3 N atoms and 3  $-\text{NH}_2$  groups in the ring. The decrease in  $\rho$  values of melamine, with the rise in temperature from 293.15 K, to 298.15 K, was  $1.18 \times 10^{-3}$ , and from 298.15 to 303.15 K, it was  $1.28 \times 10^{-3} \text{ g cm}^{-3}$ , respectively. Thus, in comparison with urea and methylurea, a larger decrease in the  $\rho$  values was noted with the rise in temperature. This proves that the thermal energy destabilizes melamine-water interaction, and thus conjugation gets activated, which weakens hydrogen bonding of melamine-water. This effect of energy on interactions of melamine was greater, which probably expanded the molecule, resulting in a decrease in the  $\rho$  values. However, like N-ureas, melamine had a greater decrease in  $\rho$  values at higher temperatures. Relevant with composition, an increase in the  $\rho$  values of urea, methylurea and melamine were found to be  $6 \times 10^{-5}$ ,  $4 \times 10^{-5}$  and  $5.7 \times 10^{-4} \text{ g cm}^{-3}$  at 293.15 K and  $6 \times 10^{-5}$ ,  $4 \times 10^{-5}$  and  $6 \times 10^{-5} \text{ g cm}^{-3}$  at 298.15 K, respectively.

Similarly, melamine at 293.15 and 298.15 K underwent an increase in the  $\rho$  values by  $5.7 \times 10^{-4}$  and  $4.8 \times 10^{-4} \text{ g cm}^{-3}$ , respectively, which shows that with its composition, the melamine underwent higher increase in  $\rho$  values than those of urea and methylurea in the order of melamine > urea > methylurea. It shows that with composition, the slightly stronger melamine-melamine interactions occurred, which resulted in increase in the intermolecular forces per unit volume, and were greater than those of urea and methylurea. It proves that with its composition, the  $-\text{CH}_3$  group inhibited intermolecular forces of methylurea. In fact, methylurea-methylurea interactions were inhibited by  $-\text{CH}_3$  group, as that of melamine and urea had greater  $\rho$  values with composition, at higher temperatures. It infers from thus observation that the  $-\text{CH}_3$  group was electron donating and hence its presence near  $-\text{NH}_2$  may inhibit the activity of lone pair of electrons of the N atom of  $-\text{NH}_2$  of methylurea. With temperature, however,  $\rho$  value weakens with composition (Table 3).

Likewise, the methylurea in aqueous urea solution produces  $\rho$  values (Table 3). That are greater than those of the aqueous methylurea and the melamine systems, which proves that urea increases the intermolecular forces of methylurea. This behaviour may be attributed to methylurea-urea interactions, in which urea may destabilize water more strongly than methylurea. The broken water may thus affect methylurea, so that urea acts as a moderator for the activity of methylurea, or for the activity of  $-\text{CH}_3$  group. This is a very significant information, which indicates that urea for solutions of N-ureas may be used as moderator for their solubilities in aqueous solutions with an additional spontaneity for structural inter-

**Table 4.** The limiting density constant ( $\rho^0$ ), the slope constants ( $S_d$ , and  $S'_d$ ), the apparent molal volume ( $V_\phi^0$ ), and the slope constants of density ( $S_v$  and  $S'_v$ ) for the least square fit of primary data of aqueous systems\*

Systems	293.15 K			298.15 K			303.15 K		
	$\rho^0$ (g cm <sup>-3</sup> )	$S_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> )	$S'_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> ) <sup>2</sup>	$\rho^0$ (g cm <sup>-3</sup> )	$S_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> )	$S'_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> ) <sup>2</sup>	$\rho^0$ (g cm <sup>-3</sup> )	$S_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> )	$S'_d$ (10 <sup>3</sup> g <sup>2</sup> cm <sup>-3</sup> ) <sup>2</sup>
Urea	1.0032	0.0119		1.0019	0.0012		1.0013	0.0112	
Methylurea	0.9983	0.0079		0.9971	0.0077		0.9954	0.0079	
Methylurea in urea	0.9984	0.0056		0.9980	0.0048		0.9960	0.0058	
Melamine	0.9980	0.0549		0.99680	0.0637		0.9950	0.0738	
NaCl				0.9979 <sup>a</sup>	0.0350 <sup>a</sup>				
				0.9980 <sup>a</sup>	0.3490 <sup>b</sup>				
	$V_\phi^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> )	$S'_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> ) <sup>2</sup>	$V_\phi^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> )	$S'_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> ) <sup>2</sup>	$V_\phi^0$ (cm <sup>3</sup> mol <sup>-1</sup> )	$S_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> )	$S'_v$ (10 <sup>3</sup> cm <sup>3</sup> mol <sup>-2</sup> ) <sup>2</sup>
Urea	44.21	0.101		44.21		0.115	44.72	0.102	
Methylurea	55.05	34.082		56.49		27.200	118.48	-963.640	3009.200
Methylurea in urea	64.40	-26.921	118.03	62.09	6.538	33.742	64.52	-40.511	165.800
Melamine	147.32	4304.100		164.49		8765.800	124.95	-1719.900	
NaCl				17.83 <sup>a</sup>	0.680 <sup>a</sup>				
				17.83 <sup>b</sup>	0.680 <sup>b</sup>				

\*superscripts a and b represent data obtained with Anton Paar and MF densimeter, respectively

actions. Thus, urea for such systems can be used as the precursor for designing the activities of the methylurea molecule.

With the increase of temperature, from 293.15 to 298.15 and 298.15 to 303.15 K, variation in  $\rho$  of methylurea in urea was  $4.1 \times 10^{-4}$  and  $1.99 \times 10^{-3}$  g cm<sup>-3</sup>, respectively. It shows that at higher temperatures, the decrease in the  $\rho$  values for this system was greater than those of the aqueous methylurea and melamine. It further indicates that this structure may decrease intermolecular forces of methylurea-urea system. However, at 298.15 K with composition, a  $3 \times 10^{-5}$  g cm<sup>-3</sup> increase in the  $\rho$  values was noted, while it remained the same with the temperature. It proves the induction of a stronger effect of composition on intermolecular interaction for ternary systems, but was weaker than those of urea, methylurea, and melamine. At higher composition, however, the higher  $\rho$  values were noted than that of urea. Thus, the presence of methylurea in the system proves that melamine-melamine interactions were greater than those of urea-urea, and methylurea-methylurea.

The values of the limiting density constant ( $\rho^0$ ) of systems determine solute-solvent interactions, which for binary systems were found in the order of urea > methylurea (in urea) > methylurea > melamine. It indicates an order of strength of interactions of the solutes with water, where melamine had weaker interactions with water. It may be concluded from this that the two free -NH<sub>2</sub> groups of urea were comparatively more active. However, when -NH<sub>2</sub> group was brought to a

different chemical environment, as in the case of methylurea, its activity was weakened. Likewise, an order of slope constant ( $S_d$ ) of  $\rho^0$  was noted as melamine > urea > methylurea > methylurea (in urea); melamine > methylurea > methylurea (in urea) > urea; and melamine > urea > methylurea > methylurea (in urea) at 293.15, 298.15 and 303.15 K, respectively. This determines the influence of compositions on molecular interactions of such systems. At 298.15 K, however, the order of  $\rho^0$  values was noted as urea > methylurea (in urea) > methylurea > melamine. This order remains the same for other temperatures. This reveals that a sequence of their interactions with water remained the same, but with compositions, it varied and indicated a weaker composition effect at each temperature. Melamine, however, had higher composition effect on the molecular interactions. Likewise, the  $V_\phi^0$  values were found as melamine > methylurea (in urea) > methylurea > urea at each temperature, which shows that the melamine had larger  $V_\phi^0$  values. Also, the  $V_\phi^0$  values of urea, with composition and temperature, varied slightly, which proves a weaker composition effect on the intermolecular forces of urea. Melamine on the other hand, showed maximum variation with composition, which is supported by the trend of their  $\rho^0$  values.

Like the  $\rho^0$  values, the  $V_\phi^0$  values of methylurea in aqueous urea were found to be higher by 10.19 cm<sup>3</sup> mol<sup>-1</sup> than those of the aqueous methylurea at 298.15 K. It decreased at 298.15 K and increased at 303.15 K. From urea to methylurea, a shift in



the  $V_{\phi}^0$  values was 10.84, 12.28 and 73.76 cm<sup>3</sup> mol<sup>-1</sup> at 293.15, 298.15 and 303.15 K (Table 3), respectively. Thus, the  $V_{\phi}^0$  values show that the contribution of -CH<sub>3</sub> with temperature was greater. It seems that the -CH<sub>3</sub> group caused greater expansion in the methylurea molecule which may be due to repulsion between electrons of the -CH<sub>3</sub> and -NH<sub>2</sub> groups. The  $V_{\phi}^0$  values of the systems at 293.15 and 298.15 K were in the order of melamine > methylurea (in urea) > methylurea > urea, but at 303.15 K, the trend was methylurea > melamine > methylurea (in urea) > urea. It shows that the -CH<sub>3</sub> group at the higher temperatures was most active, which may be due to hydrophobic interactions with itself due to the presence of -CH<sub>3</sub> group. Urea increased the  $V_{\phi}^0$  values of methylurea from aqueous to aqueous methylurea as 9.35 at 293.15, 5.6 at 298.15 and 53.96 cm<sup>3</sup> mol<sup>-1</sup> at 303.15 K. Thus, at lower temperature, urea strongly activated methylurea. With temperature, however, its activity decreased confirming a stronger structure-breaking influence of -CH<sub>3</sub> group at higher temperature (Table 3). Similarly, the  $S_v$  values with temperature were found to be in the order of melamine > methylurea > urea > methylurea (in urea); melamine > methylurea (in urea) > methylurea > urea; and urea > methylurea (in urea) > methylurea > melamine at 293.15, 298.15 and 303.15 K, respectively. Thus, melamine, in composition, developed stronger interactions at 293.15 and 298.15 K, whereas at higher temperature the interactions were weaker than those of the N-ureas. Thus, the temperature had the most effective role for the investigation of molecular interactions of systems with -NH<sub>2</sub> group. This may explain the abnormal phase behaviour of aqueous triethylamine with temperature, which proves that the trends of interactions may be useful for understanding the interaction mechanism of the electron donating behaviour of such systems and for moderating the interactions to any desired molecular level by such additives.

Similarly, the  $V_{\phi}$  values of NaCl increased with molality, which may be used to understand the cosphere overlap model in which the effect of overlap of hydration cospheres is destructive. Accordingly, the cospheres of two ionic species show an increase in volume, whereas overlap of hydrophobic-hydrophobic groups and ion-hydrophobic groups result in a decrease. Thus, the  $V_{\phi}^0$  explains the contribution of van der Waals volume ( $V_{vw}$ ), volume voids ( $V_v$ ), or empty space and volume due to shrinkage ( $V_s$ ), due to an electrostriction of solvents caused by hydrophilic groups as  $V_{\phi}^0 = V_{vw} + V_v - V_s$ . The methylurea in water decreases the extent of electrostriction caused by urea and results in a decrease in the shrinkage of the volume, assuming that the values of  $V_{vw}$  and  $V_s$  are not significantly affected by urea, an increase in the  $V_{\phi}^0$  values is noted, and the water in overlapping cospheres is more structured than that of the bulk. When this water relaxes to bulk, a decrease in volume occurs.

## Conclusion

The -NH<sub>2</sub> group of the organic compounds was noted to affect the solute-solvent interactions, whereas the -CH<sub>3</sub> group also caused an additive effect to the interacting strength of -NH<sub>2</sub> group with water. Urea was noted to enhance the densities of methylurea solutions with stronger methylurea-urea interactions. The new instrumental set-up of MFD was observed to be effective for measuring the densities of the molten salt solutions, the on-going hydrolysis process, interconversion products, equilibrium systems, polymerization, and glassy liquids at transition temperatures.

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